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Studies in the Coking of
Coal at low Temperatures

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STUDIES IN THE COKING OF COAL
AT LOW TEMPERATURES

BY

HUBERT LEONARD OLIN
A. B. University of Iowa, 1908

THESIS

Submitted in Partial Fulfillment of the Requirements for the

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Hubert Leonard Olin

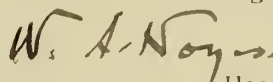
ENTITLED **Studies in the Coking of Coals at Low Temperatures.**

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF **Master of Science**



In Charge of Major Work



Head of Department

Recommendation concurred in:

} Committee

} on

} Final Examination

INTRODUCTION

Coal is the most widely distributed and by far the most abundant fuel of the world. Its greatest use is as a source of energy for industrial processes but it also serves a much wider range, from the mere matter of furnishing a heat supply, to the requirements of metallurgy and electricity. This wide variety of needs has prompted a very considerable development in the matter of modifications of the crude fuel to meet specific needs. Thus when consumers, realizing the disadvantage of handling worthless foreign matter, began to demand clean coal, mine operators responded by installing slate pickers and coal washers. Then special furnace construction required a certain uniform size of lump and the screen was brought into use. Now, in the case of the anthracite industry at least, each grade from egg to rice supplies a definite want and has a definite place on the market. In like manner schemes for briquetting were devised to adapt certain kinds of fuel such as the lignites, of little value in their natural states, to practical needs.

With the advent of the gas engine has come a demand for a gaseous fuel suitable for use in power production, and gas producer operators, now dependent largely upon anthracite, are deeply concerned over the problem of so modifying bituminous coal as to make it a possible substitute for the more expensive Eastern coal. Likewise in the field of metallurgy, wood charcoal was for a long time supposed to be the only fuel suitable for iron smelting. Its high cost, however, led smelters to look for a cheaper substance of equal calorific value. Raw coal was found to be unfitted for this purpose and not before the discovery and development of the coking

process did the iron industry come into its own. Then followed a series of improvements in methods of coke manufacture, with a rising scale of economy, from the simple smoldering earth-covered coal heap to the bee hive oven, and finally to the modern by-product plant.

It is apparent, therefore, that with the problem of adapting coal to new uses, is associated the closely related one of increasing its efficiency, and because the coking process with its ability to meet modern conditions of economy seems to offer the best solution to both problems, it is evident that the greatest development in the matter of preparation of fuels is to take place along this line. Hence there is a fundamental necessity for study in connection with that topic. This is emphasized further by the fact that as at present carried out no methods are available for bringing into line for this treatment, the coals of the Illinois type. Government reports show that Illinois, in 1909, although producing 51,000,000 tons of coal¹ and 425,000 tons of coke², manufactured only 629 tons¹ of coke from Illinois coal. Similar reports come from Ohio and other central states.

In taking up the study of the coking of coals the processes involved divide themselves naturally into two phases - the decompositions and products resulting from moderate or low temperatures and those occurring at higher temperatures. For several

1. Mineral Resources of the U. S. 1909, p. 113 (1911)

2. Engineering and Mining Journal. 91, 101 (1911)

reasons the first division of the subject offers a particularly favorable field for investigation.

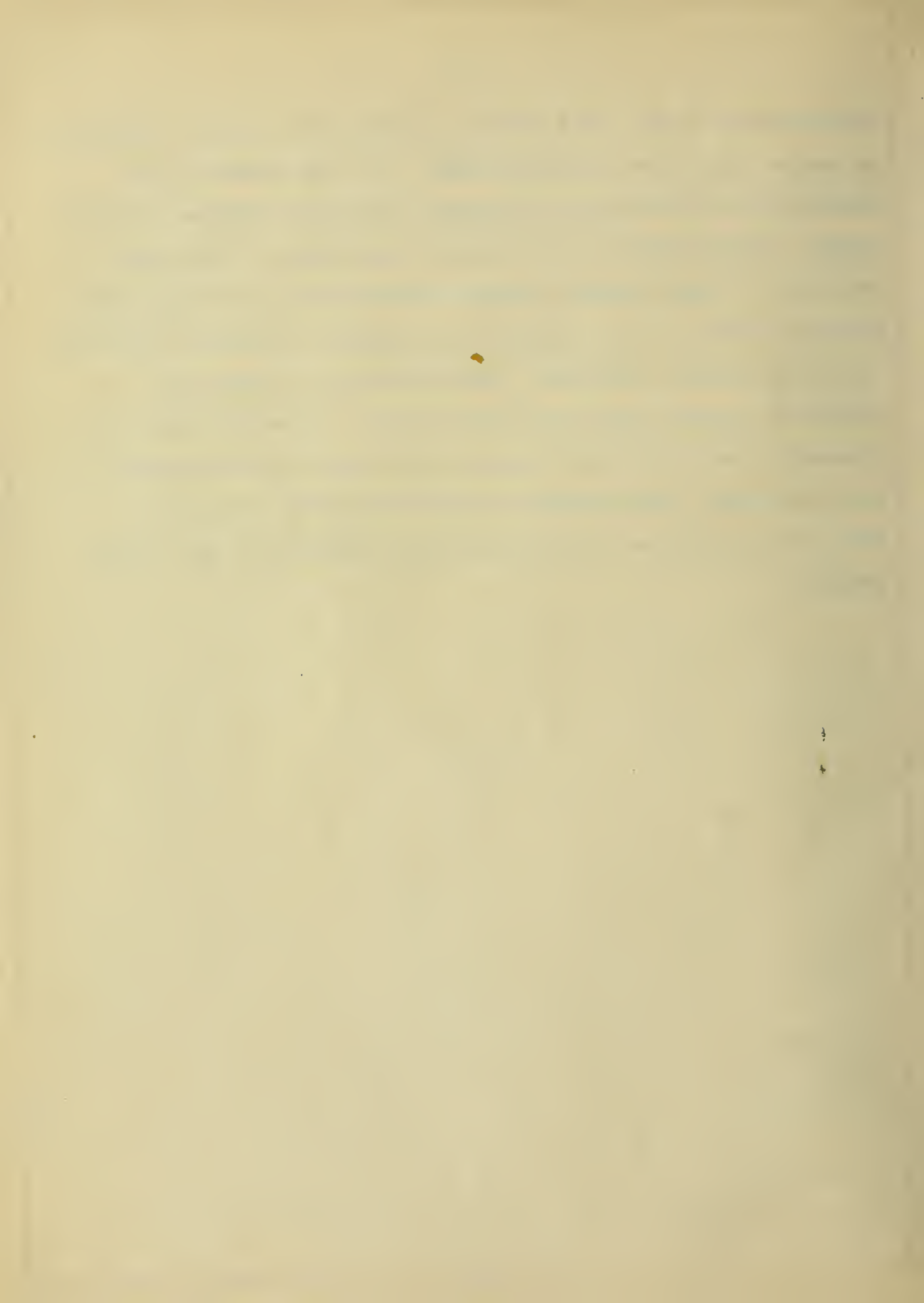
In ordinary boiler firing the loss of volatile matter, through incomplete combustion with the consequent lowering of the efficiency of the coal, is enormous. Further, the accompanying smoke is not only disagreeable and unsanitary but its production is in many places penalized by city ordinance. Low temperature distillation, by removing the smoke producing elements of the coal, promises a possible solution to this phase of the problem.

In the realm of gas manufacture, for a hundred years it was assumed that high temperature methods were the most suitable and economical. In-as-much as the character of both coke and by-products is a function of the temperatures at which they are produced, the final settlement of the question seems to demand further investigation under varying conditions. Another vast, almost untouched, field is the study of low temperature tars and oils. Just enough has been done along this line to show that these products differ radically from those evolved at high temperatures and that they give promise of assuming considerable industrial importance.

Finally, success in the coking of coals of the Illinois type can come only through an exhaustive study of the principles of coking in general and since changes in the composition of a coal begin at very low temperatures and these early modifications are probably by far the most important in determining the character of the residue, it is evident that studies must be made at all stages of heating.

A broad view of the subject therefore must include a

consideration of all its economic and scientific phases. These may be grouped under the following heads: (1) The character and composition of the volatile products evolved at different temperatures. (2) The physical and chemical properties of the solid residues. (3) The chemical changes taking place in the coal under varying conditions. (4) Chemical and physical conditions affecting the coking process directly. These subjects of course are intimately related and overlap each other. For convenience in discussing the literature bearing on the topic we have divided it into two parts, that dealing especially with low temperature distillation and that having particular reference to the coking problem.



HISTORICAL

I. Studies in the Low Temperature Distillation of Coal.

Researches in the low temperature distillation of bituminous coals have been carried on at the University of Illinois by Professor Parr³ since 1902. His ultimate aim has been to so modify the coals of the Central, Western type as to obtain a product approaching anthracite in general character and which, by virtue of its high fixed carbon content and freedom from smoke producing elements, could compete with eastern coals.

The advantages, he says, resulting from such a process can hardly be overestimated. In freight charges alone, the saving would be enormous. Assuming that the gross weight of the coal could be reduced one-fifth and that the annual shipment from Illinois points is 30,000,000 tons*, at an average rate of 50¢ per ton the saving to this state alone would be \$3,000,000. Another even more important result would be the elimination of smoke in the process of combustion, with the attending conditions of increased efficiency and lessened contamination of the atmosphere.

In a series of preliminary experiments on heating the coal to temperatures ranging from 250° to 500° for periods of less than an hour, he found that the percentage of fixed carbon was increased by more than 25% and that there was a corresponding decrease in volatile matter to a point where the formation of smoke was prevented altogether.

3. Ill. State Geol. Survey Bull. No. 4, p. 197. (1906).

*Illinois produced over 50,000,000 tons in 1909.

In order to eliminate so far as possible those variables which would result from oxidation, Parr and Francis⁴ in continuing this work heated the coals studied in nonoxidizing atmospheres. Choosing first, nitrogen as the most suitable medium for this purpose they made a careful study of the quantity and composition of the gases and heavy residues produced at different temperatures below 400°. With a view to securing an absolutely inert atmosphere and finding that the ordinary commercial nitrogen was contaminated with oxygen, they next displaced the air in the retort with steam.

The coals heated in these media, they report, underwent changes which rendered them smokeless in ordinary combustion but on account of their lack of cohesion they would need to be subjected to the briquetting process. It should be noted, however, that the constant rotation of the retort during the distillation, which was necessary in order to equalize temperatures, would tend to prevent any cementing of the original particles. References to this phase of the problem which is of prime importance will be taken up in our later discussions.

On account of the loss of water during the heating the calorific values of the residues are higher than those of the original coals but when calculated to unit ash are decidedly lower, the loss being due to the escape of the volatile hydrocarbons. On the unit coal basis the residues are again in the lead and the authors suggest that this may be explained by assuming that the volatile matter driven off contained a larger percentage of non-combustible material, e.g. water of composition and carbon dioxide, than of hydrocarbons.

In the course of some of their experiments with oxygen

4. Bulletin 24. Eng. Expt. Station. Univ. of Ill. 1908.

for the atmospheric medium they observed at unexpectedly low temperatures, rises in the thermometer readings seemingly independent of the amount of external heat supplied. This suggested to them the idea of a second series of tests entirely separate from the first, to determine the temperatures at which oxidation begins. Their method of procedure was to allow ^{the retort} to cool slowly until a drop of, say, 50° had been recorded. Oxygen was then admitted and the resulting temperature was noted. A rise was considered proof of oxidation. This was repeated until a point was reached where no rise in temperature occurred on the readmission of oxygen. In this way they found that pulverized bituminous coals in pure oxygen began to oxidize at about 125° and that they ignited at about 160°. With diluted oxygen the temperatures were somewhat higher.

While making some of their tests with atmospheres of steam they observed that near the temperature of 315° the mercury made an abrupt rise incommensurate with the amount of external heat added. After allowing the coal to cool to 300° and then again heating up to 315° they observed the same phenomenon. No appearance of carbon dioxide accompanied this sudden rise and they suggest as a tentative explanation that it was due to the exothermic character of the decompositions occurring at that stage.

Constam and Schläpfer,⁵ publishing under the title of "Studies in the Gasifying of the Principal Types of Coal", report that the percentage of oxides of carbon included in the gases given off in distilling coal varies with the oxygen content of the coal itself.

5. Jour. Gasbel. 49, 741, 774. (1906).

In considering the subject of oxidation temperatures the work of Parr and Barker⁶ on "The Occluded Gases of Coal" is of direct interest. They found that freshly mined coal immediately begins to exude hydrocarbons and to absorb oxygen and that it retains its avidity for oxygen for an indefinite length of time. The exact result of this absorption was not fully determined but it seems probable that under favorable temperature conditions it would tend to hasten combustion. This property of coal bears also a close relationship to its coking qualities and we shall refer to it later in our paper.

R. T. Chamberlain⁷ studying the causes of mine dust explosions found that fresh coal absorbs a large quantity of oxygen but that even under a vacuum it gives off very little of it. He determined further that coal bottled in air for several weeks yields some carbon dioxide but an amount equivalent to only a small part of the oxygen absorbed. This may be due to the presence of unsaturated compounds in the coal, which form addition products with oxygen.

Mahler and Charion⁸ found that when dry air was passed over pulverized coal at temperatures below 100° measurable quantities of water, carbon dioxide, and carbon monoxide were given off. Between 125° and 200° the liberation of water was so greatly accelerated as to indicate the splitting off of water of constitution. Above 150° the water contained considerable quantities of acetic acid - from

6. Bull. No. 32. Ill. Eng. Expt. Station. (1910).

7. Bull. No. 383. U. S. Geol. Sur. (1909).

8. Compt. rend. 150, 1521, 1604. (1910).

20% to 40% of the total condensate - and showed, in addition, traces of acetones, aldehydes, and methyl alcohol. The upper limit of temperature in their studies was 200°.

Porter and Cvitz⁹ made an extended study of the volatile matter of coal with a view to determining the influence of the gas composition factor on the efficiency in the use of coal in various industrial processes with special reference to gas producer, coke oven, and gas retort operation.

Their investigations show that the composition of the volatile matter of a coal depends largely upon the character of the coal itself. The gases from the younger coals of the West compared with those from the coals of the Appalachian region have high percentages of carbon dioxide and carbon monoxide. Because of the readiness with which these gases are given off even at comparatively low temperatures (300° - 500°) the authors conclude that these western coals contain compounds having a direct carbon linkage such as the complex alcohols, aldehydes, and acids. They show, further, that contrary to the theory of Dulong, who assumed that in combustion all the oxygen of a coal combined with hydrogen, in the case of certain low grade highly oxygenated coals nearly two-thirds of the oxygen appears in the volatile products in union with carbon, and that this fact accounts for the discrepancy between the determined heat value and that calculated by Dulong's method.

Higher hydrocarbons such as ethane are produced in greatest abundance from the eastern coals and they, consequently, yield more smoke in combustion. In general, however, the gas evolved from any

9. The Volatile Matter of Coal. Bull. 1, Bureau of Mines, 1910.

coal subjected to moderate heat only, is rich in the higher paraffins such as ethane and propane. In the case of Connellsville coal, at furnace temperatures of 500° and 600° these higher hydrocarbons constitute about 50% of the total paraffin content. At about 800° the percentage reaches a maximum, when it rapidly falls on account of decomposition by heat.

They conclude that the nature of the volatile products distilled from coal in the early stages of heating varies in accordance with the smoke producing tendencies of that coal. They include among the smoke producing constituents, tar, benzene, ethylene, and the higher homologues of methane.

E. Boernstein¹⁰ subjecting eight Westphalian coals to a maximum temperature of 450°, reports that the gaseous products of distillation did not exhibit differences corresponding with those shown by the different coals. Compared with ordinary coal gas, they were characterized by a higher content of heavy hydrocarbons (5% - 14%) and of methane and its homologues (55% - 76%), and a lower content of hydrogen (5% - 16%). The tars had a specific gravity between .95 and .98, began to distil at about 70° - 80°, and were found to contain no aniline, thiophene, naphthalene, or anthracene. He states that the paraffin content ranged from .3% to 2% (m. pt. 55° - 60°). He gives no further information concerning its composition.

Inasmuch as in modern gas retort operation portions of the coal do not reach their maximum temperature for one or two hours, the subject of low temperature distillation is of real importance

10. Jour. Soc. Chem. Ind. 25 - 213. (1906)

to the gas industry. In a paper read before the Michigan Gas Association, White, Park and Dunkley¹¹, report the results of their studies of the primary reactions involved in heating American coals to 500°.

Gas evolution commences only above 300° and that given off in the 300° to 350° interval contains from 25% to 40% of ethane. Above the latter point the yield of ethane diminishes and very little is produced between 450° to 500°. The illuminants decrease with increasing temperature starting with 8% at 300° and going down to zero at 500°. Methane starting with small amounts reaches its maximum in the 400° - 450° interval. They call attention to the similarity of the gases produced at low temperature to natural gas and suggest that the latter was also produced at low temperature. They give the following results of analyses:

TABLE I.

Average Yield and Composition of Gas from Coal Heated for Six to Eight Hours at Temperatures of 300° - 500°.

Vol. cu. ft. per lb. of	Pittsburg, Pa.	Bay City, Mich.	Zeigler, Ill.
Coal	1.42	1.15	0.63
CO ₂	2.9	16.2	13.1
Illum.	2.2	4.1	1.6
CO	6.2	5.0	5.8
H ₂	26.3	16.4	13.9
CH ₄	47.0	37.8	38.0
C ₂ H	13.2	11.8	19.5
N ₂	2.7	9.1	7.8
Calculated B.T.U.	902	778	871

The apparent similarity between the gases evolved from coal at low temperatures and natural gas, gives special interest to the work of Cady and McFarland¹² on the composition of the natural gases of Kansas. They proved the presence of paraffins heavier than methane and ethane, by condensing higher boiling hydrocarbons along with the methane in a bulb surrounded with liquid air. Some of these remained liquid up to ordinary temperatures and had an odor similar to that of light boiling petroleum distillates. The quantity of this residue varied in the different gases.

Professor V. B. Lewes¹³ in discussing the relative merits of high and low temperatures for gas distillation, gives parallel tables showing the net cost of 1000 cu. ft. of gas produced by each of the two processes.

TABLE II.
Cost of 1000 cu. ft. of Gas.

(1) High (900°)		(2) Low (400°)	
	d.		d.
Coal	13.30		26.50
Operating expenses	<u>6.74</u>		<u>5.50</u>
	20.04		32.00
Less Value of Residuals Produced.			
Coke	.82 cwt. 6.11	2.4 cwt	17.64
Tar	.9 gal. 1.30	4.6 gal	6.90
NH ₄ products	<u>2.11</u>		<u>2.80</u>
	9.52		27.34

11. Am. Gas Light Jour. 89 - 621. (1906)

12. Jour. of Am. Chem. Soc. 29, 1523. (1907)

13. Engineering. 85 - 410. (1908)

Net Cost of Gas

10.52	4.66
B.T.U. of gas 592.	750.

He points out that although the coke residues are figured at the same price, coke (2) is really more valuable since it contains 15% of volatile matter which increases its calorific value. He states also that the low temperature tar distillates contain valuable fractions of a character different from those obtained from ordinary gas tar, one of which is a distillate especially suitable for use in motors.

Burgess and Wheeler¹⁴ working on the problem of the prevention of mine dust explosions and recognizing the relationship that exists between the character of the volatile matter escaping from a heated coal and its degree of inflammability, studied the composition of the gases evolved at different temperatures.

They found that with all coals whether bituminous, semi-bituminous, or anthracite, there was a well-defined decomposition point at a temperature between 700° and 800° which corresponds with a marked increase in the quantity of hydrogen evolved. This increase they attribute to the thermal decomposition of one or more of the higher homologues of methane yielding hydrogen and carbon. Ethane, propane, butane, and, probably, higher members of the paraffin series form a large percentage of the gases given off at temperatures below 450°; above 700° they no longer appear.

They believe that the smoke producing elements consist almost entirely of the higher paraffins and differ from Porter and

14. Jour. Chem. Soc. 97 - 1917. (1910)

Ovitz in excluding ethylene and the related unsaturated gases from this class. This view is based upon experiments they made showing that ethylene decomposing at 600°, deposited very little carbon.

A typical analysis of the gases they obtained is given below.

TABLE III.

Gas from Coal from Abertillery, South Wales (Bituminous)

Coal (C)	Temp.	Illum.	CO ₂	CO	H ₂	CH ₄	C ₂ H ₆
	500°	5.8	3.9	4.7	8.0	64.5	11.0
	600°	4.9	3.2	6.4	25.0	47.2	12.4
	700°	2.8	3.4	7.4	34.7	46.2	4.2
	800°	2.8	2.5	9.8	50.8	28.6	4.7
	1100°	4.2	1.4	13.0	60.7	18.8	1.8

G. E. Davis¹⁵ discussing the tars formed under different conditions says that at low temperatures are produced mainly such hydrocarbons as belong to the paraffin series having the general formula C_nH_{2n+2} , along with the olefines C_nH_{2n} . The lower members of these series are liquid, and, furnished in the pure state, are illuminating and lubricating oils; the higher ones are solid and form commercial paraffin. They are always accompanied by phenols. Liquid products prevail and among the watery ones acetic acid predominates.

If on the other hand, the coal has been decomposed at very high temperature, the molecules are grouped quite differently. While olefines and acetylenes occur more or less the paraffins disappear almost entirely with the resultant deposition of carbon.

15. Jour. Soc. Chem. Ind. 5, 2. (1886)

Some of this carbon set free is deposited in the retort in a compact graphitoidal form; some occurs in a state of extremely fine division in the tar and forms a constituent of the pitch or coke remaining behind. At the same time the action of heat effects molecular condensations by which process compounds of a higher molecular weight are formed, as naphthalene, anthracene, and phenanthrene.

Behrens¹⁶ found that the tar obtained in the distillation of coal in the ordinary fire-clay gas-retorts (operated at high temperatures) was much richer in benzene, toluene, naphthalene, etc., than the tar made in Pauwel's coke ovens (operated at low temperatures) from the same kind of coal.

Lunge¹⁷ thinks that at low temperatures most of the nitrogen appears in aniline and fatty amines (ethylamine, propylamine, amylamine); at high temperatures in the pyradine bases, along with picoline, lutidine, viridine, etc. He admits that it needs verification by more detailed investigations. In general, at high temperatures the tendency to complete dissociation becomes far more pronounced; the products approach more and more to free carbon on the one hand and free hydrogen on the other.

Watson Smith¹⁸ states that naphthalene increases with rise of temperature, also anthracene, which is then found in the creosote oil coming over before the anthracene oil proper. Carbolic acid is also an important constituent.

16. Dingler's Polyt. Journal. 208, 362.

17. Coal Tar and Ammonia. p. 26, (1900)

18. Jour. Soc. Chem. Ind. 8, 950. (1890)

II. Studies in Conditions Affecting the Production of Coke.

It has been said that "the question as to what really is the factor that produces the coking tendency characteristic of some coals has been a matter of speculation among manufacturers and users of coke for the past two hundred years and that we are apparently no nearer to its solution now than were the investigators of two centuries ago".

"What is it that determines the coking of coal?" says Dr. W. B. Phillips¹⁹ in pointing out the difficulties of the problem. "It is impossible to answer this question fully for we do not yet know what coal itself is". He refers to the fact that a knowledge of the ultimate composition of coal throws little or no light upon the way in which the elements are combined among themselves. Further "the behavior of isomeric chemical compounds under the action of the same reagents cannot be foretold even when they are of simple constitution. As we ascend the scale of complex compounds the difficulties of deciding why thus and so is possible and actual, become more and more evident, and when we arrive at such a compound or mixture of compounds as coal, we are wholly unable to assign a formula or group of formulas to it. Not knowing its chemical nature we are not able to say what compounds take part in the coking process except that they are probably of the bitumen group".

F. C. Keighley²⁰ argues that since the chemical constituents of coals from any horizon are not necessarily indicative of their coking properties, it is reasonable to assume

19. American Manufacturer. Dec. 16, 1898. p. 883.

20. Iron Age. 80 - 364. Aug. 1907. Mines and Minerals Oct. 1907.

that an important factor determining the coking quality must be one of a physical character and not altogether chemical.

It is known, he says, that the finest coking coals not only are of the bituminous class, but their structure is such that upon fracture they exhibit a fingery or prismatic form and separate vertically, while the more difficult coking coals and the ones of a bituminous character that cannot be coked at all, are of a laminated structure and upon fracture break into cubical form and have a tendency to separate horizontally instead of vertically. This he thinks would indicate that the coking property depends very largely upon the arrangement of the small particles of coal composing the seam. If these lie in the seam with their longer axes horizontal to the bedding of the seam they are unfavorable to the coking process. On the other hand, if they are perpendicular to the strike of the seam, i.e., at right angles with its bedding, the coking tendency is much more pronounced. He suggests that the superiority of Connellsville coke may be due to the structure given it in the process of formation by the peculiar geological movements of the region in which it is found.

He compares two types of coal, the first, Connellsville, a good coking coal, neat-crystalline in structure, with the Brier Hill, a non coking laminated coal. In discussing the latter he points out that it is made up of two different substances; that the laminae are alternately bright and dull. The bright portion is composed of extremely rich bituminous coal, the dull, of fine black powdery material that is almost pure carbon. This mineral charcoal is not only devoid of fusing or cementing properties itself but acts as a separating wall to prevent the bituminous

layers from fusing.

M. A. Pishel²¹ suggests a simple practical test for coking coal. Pulverize the coal to 100 mesh in an agate mortar. Pour out the dust and observe its condition. If it adheres strongly to the mortar it will probably make good coke, he says. If there is little adhesion, coking properties are absent. In his experimental work he tested more than 150 different specimens. Of the four Illinois coals tried, none stuck to the mortar while most of the Eastern coals adhered. He offers no theory to account for this phenomenon.

Groves and Thorp²² classify coals with respect to their coking properties as sand coals, those devoid of coking powers; sinter coals, those possessing it to a relatively slight degree; coking coals, those which produce a good quality of coke; and anthracite.

They give the following analytical tables made up from the work of Richardson, Regnault and others:

TABLE IV.

	(percentage)		
	C	H	O
Sand coal	77	5	18
Sinter coal	83	5	12
Coking coal	87	5	8
Anthracite	95	3	2

TABLE V.

Anthracite	$80C + 88H + O$
Blazy sinter	$80C + 128H + 60$

21. Econ. Geol. June - July 1908. p. 265 - 270.

22. Chem. Tech. Vol. 1, p. 122 (ed. 1889)

Lancashire cannel sinter	80C + 128H + 30
Mons coking	80C + 24CH + 50
Grand Croix-highly coking	80C + 112H + 30

It will be observed from Table II that the amount of hydrogen in the first three varieties is identical, while the oxygen diminishes as the coking property is developed. The Grand Croix coal (Table V) has only half the amount of hydrogen contained in the coking coal from Mons. Anthracite, consisting almost entirely of carbon, may be considered a kind of natural coke.

They state in conclusion, however, that Stein of Dresden has shown that coking and non-coking coals may have the same ultimate composition and that simple analyses, therefore, cannot determine absolutely the coking property of the coal. They suggest that the real source of coking lies in a resinoid body or bodies identical in composition with the coke itself.

White and others¹¹ mention the work of Ste. Clair Deville, Consulting Chemist of the Paris Gas Company, who, basing his conclusions on the results of nearly 2000 tests, divided coals into groups according to the relations of their percentages of oxygen to hydrogen. He found that all coking coals contain a percentage of oxygen approximately twice that of hydrogen.

They reasoned that possibly the artificial application of heat which gives as its first products, water and other compounds rich in oxygen, would lower the relatively high oxygen of the non-coking coals and possibly bring them into the coking class. They found, however, that coals which were originally non coking were

11. Am. Gas Light Jour. 89 - 621. (1906)

not improved in this respect even though the oxygen-hydrogen ratio was brought down to 2 to 1. The coking coals tested sintered together during the heating and if the resultant mass was heated to redness it retained its shape and gave a good coke. If, however, it was powdered before it remained a powder.

Dr. Haberman²³ in studying the spontaneous heating of coals noted the fact that long storage tends to destroy both gasifying and coking values. He found that those coals that oxidized the most and gave the greatest rise in temperature absorbed the largest quantities of bromine.

Professor Fischer²⁴ of Göttingen working on the same problem mentions the loss of coking suffered by oxidized coals. He too suggests the bromine absorption test for determining the chemical activity of the fuel.

Parr and Lindgren²⁵ doing work on the weathering of coal at the University of Illinois observed that samples exposed for several months gave powdery residues instead of the coke left by fresh coals.

In connection with the foregoing it is interesting to note that an Englishman has recently taken out a French patent²⁶ on the treatment of coal for the manufacture of a better quality of coke and illuminating gas whereby oxidants are added, e.g., for 1000 kg. of coal, 165 parts of $KClO_3$ to 5 of $KMnO_4$ ". This would

23. Schillings Jour. für Gasbel. 49 - 419. (1906)

24. The Gas World. April 13, 1901.

25. Unpublished reports of supplementary studies to Bull. 17, Ill. Eng. Expt. Sta. (1911)

26. French Patent 390,509. (1910)

seem to be contradictory to the results obtained by practically all other investigators.

David White²⁷ in his bulletin "The Effect of Oxygen in Coal" after discussing the negative calorific value of the oxygen and the transition between various grades of coal due to progressive devolatilization brought about more or less directly by dynamic forces, takes up a study of the relative proportion of oxygen, hydrogen, and carbon, in coking coals with special reference to a theory framed to explain the coking quality.

He mentions the work of Regnault²⁸ and Bertrand²⁹ who found that the high percentage of volatile matter and the high illuminating value of certain bogheads and oil shales are due to the presence of immense numbers of supposed gelatinous algae which, in these coals, seem to have exercised a selective attraction for certain bituminous compounds. Likewise the conditions of accumulation and deposition attending the origin of many coals were doubtless favorable for the mingling of algae and different animal remains, with the debris of higher plant types.

Mr. White thinks it is more than probable that the substances of these lower organisms contributed as ingredients to the mass of coal forming material, and that they, therefore, exerted some influence on the character and quality of the final residues. He considers the higher percentage of bituminous matter in the older and more altered condition of the fuel, due to concentration as the

27. Bull. U. S. Geol. Surv. No. 382, 1909.

28. Regnault, B. Les micro organismes des combustibles fossiles, St. Etienne, 1903.

29. Bull. Soc. d'hist. Nat. Autun. Vol. 9, 1897, p. 193.

result of devolatilization of the coal by dynamochemical processes, the larger part of the concentration being the result of loss of oxygen, this loss being disproportionally great as compared to that of hydrogen. Thus the progressive deoxygenation of the organic matter accomplishes bituminization.

Now, he continues, the qualities of fusibility and swelling concurrent with bituminization which appear to characterize fuels known to contain quantities of gelatinous micro-algae, are also necessary to the coking quality in coals, and he thinks it permissible, therefore, to inquire whether the coking property may not be due to some unascertained proportion of gelatinous algal matter entering into the original mass from which the coal was formed and imparting to it this fusibility and tendency to swell.

While the presence of micro-algal ingredients has been noted in peats and even in some brown coals, yet it is very evident that their detection by microscopical means in the highly metamorphosed coking coals is so difficult as to be practically impossible. The evidence of chemical analysis must, therefore, be called into service. The coals, he says, whose large volatile combustible matter contains relatively the highest hydrogen and the lowest oxygen, thus approaching nearest the bitumen analyses, are those in which the organic remains described as micro-algae are most predominant and best preserved. If then, in the high volatile coals high bituminization and gelatinous algal ingredients go together and the presence of the latter causes the coal to fuse and swell, we may conclude that high volatile coals that show sufficiently high bituminization will coke by the ordinary process.

The degree of bituminization is indicated by the relative excess of hydrogen as compared with the diminished oxygen in dry coal and is expressed by the ratio H : O.

Data covering the tests of over 300 coals from different localities furnished by the U. S. Geol. Survey are given. It was found that those coals having a H : O ratio of 59 or more, coke by the ordinary commercial process. Nearly all below 59 and above 55 so far as tested, make a coke. Those below 55 usually give a poor and dark product. The best cokes obtained by the ordinary process were made from coals having a ratio of 60 or over. It was noted however that with coals with a fixed carbon value of over 79% the rule breaks down.

He remarks that his hypothesis appears to harmonize with the tendency of coking coals to cohere when reduced to fine powder, discussed by M. A. Pishel²¹.

O. Boudouard³⁰ took up the study of coals with the specific purpose of determining the causes of coking and selected for experiments samples of (1) English anthracite, (2) Courrieres (1/4 bitum), (3) Belgian forge coal, (4) Forge coal of unknown origin which had lain in the laboratory several years, (5) Bruay (3/4 bitum), (6) Coal of unknown origin, (7) Lignite.

The following table gives the results of the approximate analyses:

TABLE VI.

	¹	²	³	⁴	⁵	⁶	⁷
Fixed carb.	88.6	89.5	70.5	79.1	39.3	51.4	37.3
Ash	2.5	1.6	4.6	2.6	3.1	2.3	4.2

³⁰. Bull. de la Sec. Chim. 5 (series 4) 365 - 380 (1909)

Vol. Matter	8.8	8.8	24.8	18.1	37.6	46.2	58.4
Character of coke	powd	powd	hard	hard	hard	slightly caked	powd.
Hardness	0	0	3	3	3	0	0

(The relative hardness of the coke is given by the figures 3, 2, 1 and 0; 3 denoting a hard compact coke, 0, a powdery residue)

These coals were successively subjected for periods of 105 hours each to the action of air at 15° and 100°. After the first treatment little change in the coal and in the appearance and character of the coke was noted except that numbers (6) and (7) showed traces of humic acid. In contrast with this, after being heated at 100°, none had retained their coking powers and all but (1) and (2) contained humic acid. A marked increase in weight due to oxygen absorption was observed, amounting in some cases to nearly 5%.

He further treated 25 gm. of each of the coals studied with 150 gm. of concentrated nitric acid for a period of 2 1/2 months. Analyses of the residues gave the following results:

TABLE VII.

	1	2	3	4	5	6	7
Percent change in weight	+15.6	+26.0	+6.4	+20.4	+17.2	-14.0	-36.8
Fixed carbon	68.1	54.7	56.5	51.5	49.6	43.2	39.4
Ash	1.8	.41	1.5	6.1	1.6	.72	.61
Vol. Matter	30.1	44.8	41.9	42.2	48.7	56.0	59.9
Appearance of coke	powd.	powd.	powd.	powd.	traces of agglom.	traces of agglom.	powd.
Humic Acid	0	0	15%	8%	50%	40%	27%

Organic solvents such as ligroin, pyridine, benzene, carbon disulphide, carbon tetra chloride and the like, modified in no appreciable way the quality of the coke produced. Concentrated sulphuric acid destroyed the coking power; concentrated hydrochloric acid had no effect.

In none of these coals did humic acid exist before treatment and since its presence was always constant in the same oxidized coals which had in the process lost their coking powers, he was led to look to the carbohydrates and particularly to cellulose for the original of the acid. He found that starch or sugar treated with bromine water, for instance, yields humic acid much like that obtained from coal.

It is probable, he thinks, that the hydrocarbonaceous substances giving rise to this acid do not exist in a single form but in a state of great condensation and polymerization is a result of the decomposition of the living matter, the principle characteristics of this series of processes being the disintegration of the plant tissues and the accumulation of carbon at the expense of hydrogen and oxygen.

In his comparative studies of natural and oxidized coals he noted that the production of a very small quantity of humic acid (less than 1%) marked the disappearance of the coking qualities of the original sample.

Dennstedt and Bünz³¹ hold with Boudouard that humic acids are the ultimate oxidation products of coals and the most inflammable coals are those that produce the largest quantities of the acid.

³¹. Zeitsch. f. ang. Chem. 21, 1825 (1908)

The exact nature and composition of the so-called humic acids, however, seems to be unknown. Boudouard³⁰ quotes the results of several experimenters who produced the substance by treating sugar with acids. The empirical formulas - no structural formulas are attempted - range from $C_{24} H O$ (Stein) to $C_4 H_{24} O_2$ (Müllder). He himself proposes $C H_4 O$ as the composition of the humic products he obtained by extracting oxidized coal with potassium hydroxide.

Henry Hennebutte³² in discussing the subject of coking states that an important factor is the coefficient of contraction. If this is not equal to the coefficient of expansion at the maximum temperature of the oven, the coke, on cooling, will have little strength and cohesion.

He has patented a process by which he succeeds in coking coals ordinarily non-coking, by adding to the coal a substance with a distillation temperature nearly equal to that at which the emission of volatile matter from the coal, ceases. Thus the volatile matter from the cementing substance filters through the coke already formed, and in so doing decomposes with the deposition of graphite which strengthens the cell walls.

30. Bull. de la Soc. Chim. 5 (series 4) 365. (1909)

32. Rev. Metallurgie 1 - 625. (1904)

Summary of Opinions.

A very brief review of the literature covering the decomposition that takes place at low temperatures in the distillation of coal, is sufficient to prove to the student that the problem in all its phases is distinctly modern. A glance at the bibliography will show that few, if any references date back more than ten years and that most of the publications on the subject have appeared within the last two or three. Indeed, Burgess and Wheeler¹⁴ writing in 1910, remark that "previous work has been very scanty". Furthermore, almost without exception, those investigators who have already made reports announce that their first articles are more or less incomplete and that they expect to continue along the same lines of study.

While the development of the subject is evidently still in its infancy, yet results from different sources are in many cases entirely consistent. Of particular interest to us, in that it bears a close relationship to the problem of smoke prevention, is the fact, mentioned by nearly all authorities, that the heavy smoke producing benzenes and paraffins of high carbon content are given off at low temperatures and are practically eliminated at 500°. Attempts to separate and estimate the higher homologues of methane contained in the early distillates however, have not been entirely successful on account of a lack of adequate methods of gas analysis. Cady and McFarland¹², using liquid air, got perhaps the best results but, even their scheme leaves much to be desired. Authors reporting the paraffin content of the gases studied therefore have been

14. Jour. Chem. Soc. 97 - 1917. (1910)

12. Jour. Chem. Soc. 29, 1523. (1907)

obliged to estimate the heavier members as "ethane", or, using the formula C_nH_{2n+2} , to give average values of n .

It is generally agreed further, that as temperatures rise above 500°, methane and hydrogen are the principal gas constituents, being decomposition products of not only the coal itself but of some of the gases given off at the lower temperatures. Below 400° hydrogen is present in very small amounts. It seems fairly well established, therefore, that the density and consequently the calorific value of a gas varies inversely with the temperature at which it is evolved and that a very moderate heating of the coal is sufficient to remove enough of the smoke producing elements to make the combustion of the residue clean and economical.

With a very small amount of work done in determining the character of low temperature tar distillates, a fruitful field is left for future investigation.

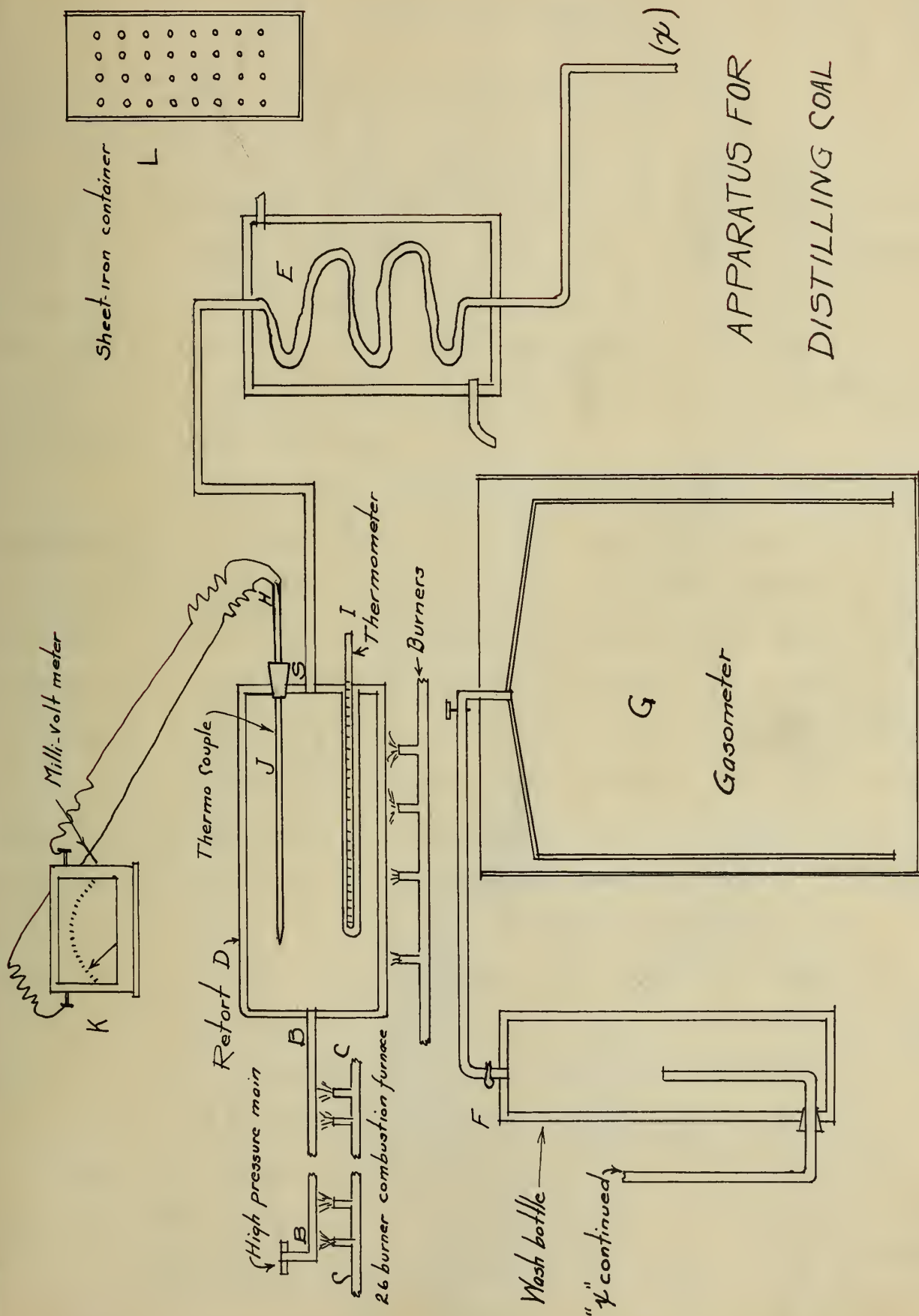
Paraffin oils, valuable for lubricating and power generating, seem to predominate, while the equally important phenol derivatives as anthracene are present to a less extent than in the high temperature runs.

The investigations of Parr and Francis coupled with the results obtained by the manufacturers of "coalite" in England prove that coal, modified by the application of moderate heat, gains valuable properties and that it retains a high calorific value.

In the use of certain types of coal, however, such as those of the central west, the problem of putting the residues into marketable condition demands a solution before the process can be made an economic success.

Much has been written in attempts to explain the causes

of coking, or at least to define the conditions that govern it. The wide divergence of many of these views puts the literature in a rather chaotic state. Indeed some of the articles cited, such as Keighley's, are reviewed for the purpose of showing that on this one subject at least authorities are likely to drift out to sea, rather than with a view to shedding much light upon the matter. Nevertheless there is harmony in aspects of the problem. On comparing the work of Parr and Barker and of Chamberlain on the oxygen absorption of coal at ordinary temperatures, and of Parr and Francis on oxidation phenomena, with that of several others who have studied the effect of weathering on coking, it is evident that the physical and chemical changes taking place at extremely low temperatures bear ~~to~~ close relationship to the character of the coke produced. In other words the first stages of heating are the critical stages. But the crux of the matter still is left. Investigators are unanimous in agreeing that a high O : H ratio marks the absence of cementation; several foreign experimentors report the appearance of "humic" acids as the cementing properties disappear through oxidation, but the exact connection between the phenomenon of oxygen absorption and that of the failure of a coal to fuse and harden into a compact mass, is still undemonstrated.



APPARATUS FOR
DISTILLING COAL

Experimental Work.

First Series: Coking Tests.

The work described in this chapter is a continuation of a series of investigations in the low temperature distillation of coal carried on by Parr and Francis in 1907 - 08. Inasmuch as a somewhat thorough study of the results obtained by using an atmosphere of steam was made at that time, steam was chosen as the medium for the present series because of its value as a heat carrier rather than for its non-oxidizing properties.

Apparatus. - BB, Plate I, is a $5/8$ in. pipe 11 ft. long, fitted with two return elbows, in which steam, admitted from the high pressure main at A, is heated by a 26 burner combustion furnace, CC. The retort D, 18" by 8', containing the coal, is fitted with a head, J, held in place with set-screws and sealed with asbestos. From the retort, a pipe conducts the distillates to a condenser E which is connected in turn with a large wash bottle, F. Here the oils and tars are collected while the gases pass on to the gasometer, G. A Hoskins nickel-nichrome thermo-couple inserted through a stuffing box, S, and joined to a Weston milli-vol¹imeter, K, measures the temperatures of the retort contents. As an auxiliary instrument a high reading thermometer sliding into a long narrow pocket P, is sometimes used. An extra quantity of heat, when needed, is supplied by a battery of burners placed directly under the retort and this is retained by means of an asbestos lined oven which entirely surrounds both.

Material. - The coals used in this series of experiments

include the following, all from Illinois mines. Names of counties from which they come are also given. New Ohio and Sunnyside from Williamson; Benton and Duquoin from Franklin; Electric from Vermilion; Harrisburg from Saline; Niantic from Macon; Majestic from Perry; and New Kentucky from Murphysboro, Jackson Ct. Results of approximate analyses are given below. It should be noted, however, that since these studies were made for the purpose of testing the coking powers of the different coals and not to determine their relative commercial values, many of the samples selected were cleaner than the general run of mine.

TABLE VIII.

Composition of Coals.

Coal	Moisture	Ash	Sulphur	B.T.U.	B.T.U. (dry)
Sunnyside	2.68	12.60	.96	12198	12534
New Ohio	6.02	11.43	1.08	11850	14569
Benton	2.29	4.40	1.37	13734	14820
Duquoin	6.08	11.86	.95	11079	12453
Electric	1.41	22.99	5.44	10695	10848
Harrisburg	5.15	7.34	1.65	13056	13774
Niantic	7.38	11.69	3.41	10989	12281
Majestic	6.41	11.26	3.23	11698	14483
New Kentucky	2.89	6.22	1.80	13317	14805

Operation, Mechanical. - A sufficient quantity of coal for one run only - from 2500 to 3000 grams - was crushed at one time. In the early experiments the size of the pieces ranged from

quarter inch down to buckwheat, dust being separated by means of a sieve. At first the coal was put directly into the retort but it was soon found that the circulation of the steam was retarded with a subsequent delay in the heating of the mass. To remedy this a cylindrical sheet iron container 6 inches in diameter, perforated with small holes, was made to hold the charge. This shell, being smaller than the retort and having a space surrounding the shell of about 1 inch thus allowed a free distribution of heat and it was used throughout the remaining runs of the series.

In putting the apparatus into operation, steam was admitted from the main and allowed to blow through the system until the air was entirely displaced. The combustion furnace was then started and, finally, the burners under the retort. The coal was not mixed or stirred after heating had begun.

The following table will give an idea of the average working conditions. It must be admitted however that on account of the great variations in the gas pressure with consequent changes in heat supply the time factor is not very significant. With increasing facilities for applying external heat to the retort the time of the later runs - (nineteen were made in this series)-was reduced to about five hours.

TABLE IX.

Test Conditions; First Series.

Run no.	3	4	5	6	7
Wt. of coal*	4800	5351	2195	3498	3398
Wt. of residue	4030	4112	1895	2810	2895
Time	8 hr.	14 hr.	9 hr.	8 hr.	9 hr.
Max. temp.	475°	515°	450°	410°	430°

* Carterville Lump crushed to 1/2 in. and smaller, was used in the

Following the experiments made under these and similar conditions, the most essential being the absolute exclusion of oxygen, the most interesting and important results of the whole work were obtained. The coal, much of which was originally rather lumpy and heterogeneous, was found to have undergone a change resulting in the fusion of the whole charge into a compact homogeneous mass. In short, the coal had coked. While this property of cementation was the most noticeable when the coal was finely crushed yet with the application of sufficient heat even the large lumps lost their identities by fusing together into one.

In order to test the effect of continuing the heating of the residues at high temperatures, about three kilos of the coke from run (8), containing 23% of volatile matter, was fired in an ordinary assay muffle at about 1200° for six hours. The muffle was imperfectly sealed and considerable oxidation took place, making the conditions unfavorable for a perfect test. Nevertheless the partial disintegration of the mass and the utter absence of even traces of re-fusion would tend to prove that the critical coking stage had been passed at the lower temperatures.

Effect of Atmospheric Oxidation.

In Run (9) the retort was charged with the 10 mesh screenings removed from the coal used in the previous runs. This material accumulating from day to day for a period of about six weeks had been stored in an ordinary coal-hod kept in the grinding room. After being heated for eleven hours under conditions identical with those of the preceding runs it showed no signs of fusing.

first ten runs. It had been delivered to the laboratory in considerable quantity a few weeks before the beginning of the work.





Coking Tests.

Fig. 1.

Numbers (1) and (2), Fig. (1) show typical residues from the coals of southern Illinois, Benton and Harrisburg, which contain relatively low percentages of volatile matter (about 35%). Their closeness of grain is in marked contract with the spongy coke, No. 3, Fig (), made from the Danville "Electric" Mine coal with 43% of volatile constituents. No. (4) is from a weathered sample of Niantic, a coal of the same type. This came from the yards of an Urbana dealer who affirmed that it had been in stock a short time only. Although it was subjected to the same treatment as No. (3) no cementation took place and it may be seen that each particle retains its initial shape. The mass is so friable that it may be crushed between the fingers.

No. (5) gives another view of a Danville Electric Mine coke which well illustrates a property this coal possesses to an unusual degree, viz., that of fusibility. The lump shown is a part of a mass that flowed out of the container, forming a bubble like puddle. It would seem, therefore, that this type of coal, ordinarily considered to be one of the ^{lower} grades mined in the state has coking qualities superior to those of many of the better grades.

On account of the hardening and setting of the coke it was found difficult to remove the thermo-couple at the end of the run without damaging it. In some of the latter tests therefore, no measurements of temperatures were made. Thermal conditions were maintained fairly constant in each case, however, ^{by} keeping the heating pipe and the bottom of the retort at a dull red heat.

The coal analyses were made according to the method recommended by the American Chemical Society. Calorific values

were determined by means of the Parr Calorimeter.

TABLE X.

Proximate Analyses of the Residues from Selected Runs.

Run	12 New Ohio	14 Harrisburg	17 Danville Mine
Max. Temp.	520°	550°	500°
Moisture	.45	.40	.90
Ash	3.0	7.0	13.0
Vol. Matter	25.0	23.0	22.0
Sulphur	.89	1.20	4.0
B. T. U.	14456	13611	12623
B. T. U. (dry)	14530	13665	12737
Spec. grav.	.652	.630	.606

The comparison of original coals with their coke residues so far as made, gave results in agreement with those obtained by Parr and Francis⁴ but no extensive work was done in this direction. In an attempt to determine whether an absolute fixation of carbon takes place analyses were made with the following results.

TABLE XI.

Comparison of Volatile Contents of Coal with Residue.
Max. Temp. 500°.

	Percentages
Volatile matter coal (11)	51.82
Less water (8.82)	43.00
V. M. residue (11)	27.95
Less water (.34)	27.61
Loss in distilling (direct weighing)	29.10
Less water (8.82)	20.28
V. M. of residue on basis of original coal	22.01
Loss (20.28) plus V. M. left (22.01)	42.29
Original V. M.	43.00

4. Bull. 24. Eng. Expt. Sta. 1908.

This would tend to show that at low temperatures at least, little or no actual deposition of carbon takes place.

First Series: Sulphur Tests.

It may be seen by referring to Table X that the sulphur content of the coke residues, especially those from coals of northern Illinois, is extremely high. Inasmuch as the iron industry demands coke with a maximum sulphur content of 1.2% it is evident that in their present condition our fuels would be unsuitable for use in smelting.

Acting on the assumption that under the influence of heat iron pyrites decomposes according to the equation



we performed some simple experiments to determine the extent to which this takes place.

Five grams of Danville Electric residue (17) coked at about 550°, with a sulphur content of 4%, was treated with a large excess of dilute hydrochloric acid. The mass was thoroughly washed and the percentage of sulphur remaining determined. Test No. (1) gave 3.55%, No. (2) under identical conditions 3.70%. Next a quantity of the same residue kept well moistened, was exposed to air and sunlight for a period of twelve days. After treatment the sulphur content was 3.74%. On the subject of the decomposition of pyrite, Peters³³ quoted Sticht as saying, "At dull red heat FeS_2 loses $\frac{3}{7}$ of its sulphur and becomes Fe_7S_8 . At 1200° it becomes for the first time, FeS ". It is evident, therefore, that the pyrite iron had been little

affected by the temperatures of the retort.

First Series: Fractionation of Tar.

The tar collected from the different runs of the series was fractionated according to the method suggested by B. Nickels, quoted by Allen.³⁴ 500 grams of the tar was placed in a large glass retort and heated with a powerful bunsen burner. The following fractions were made (1) ammoniacal liquor, (2) light oils, (3) heavy oils, (4) creosote oil, and (5) pitch. The collecting of the "light oil" was continued until a drop of the distillate sank in water. The crystallization of the syrupy liquid on a cold knife blade marked the end of fraction (3) and the remaining volatile matter was lumped as number (4). The hard black residue was classed as pitch.

Based on this scheme the result of the distillation was as follows:

TABLE XII.

Fractions from Low Temperature Tar.

Water	100°	5%
1. Light oils		25%
2. Heavy oils		28%
3. Creosote oils		22%
4. Carbon		20%

For the purpose of comparison we quote the following values which Lunge³⁵ says represents the average composition of high temperature tars.

34. Commercial Organic Analysis. Vol. II, p. 52.

35. Crookes and Fischer Manual of Chem. Tech. p. 507 (1892)

TABLE XIII.

Fractions from High Temperatures Tars.

1. First runnings	24 - 3.5%
2. Light oils	6 - 6.7%
3. Heavy oils	30.4%
4. Hard pitch	55%

It will be seen that the first has a much lower percentage of the comparatively valueless pitch and a correspondingly higher content of the light oils, than the second.

The "light" and "heavy" oils, (1) and (2), darken when exposed to the air, presumably from oxygen absorption. The first has an iodine number of 90, the second 124. The creosote oil has the viscosity of ordinary molasses at room temperatures.

No attempts were made to determine the composition of the different distillates but the problem will, no doubt, be taken up in this laboratory in the near future.

First Series: Study of Gases.

The methods of Hemple were used in making all gas analyses. For absorbing the illuminants, bromine water was found to check with the results obtained when fuming sulphuric acid was used and was free from some of the annoying properties of the latter. The paraffin hydrocarbons were determined by the use of the explosion pipette. Hydrogen was determined separately with palladium sponge, a variation from the ordinary industrial method that is absolutely necessary when higher paraffins are present in the gas. Calorific values were determined with the Parr gas calorimeter.

It is impossible to determine, absolutely, the paraffin content of a gas by any methods now in general use when the number of the higher homologues of methane present is unknown. By assuming, however, that they are all "ethane", an average value may be obtained by the explosion pipette method by solving these simultaneous equations:

$$\text{Vol. contract.} = 3/2 (\text{H}_2) + 2\text{CH}_4 + 2 \text{ } 1/2 (\text{C}_2\text{H}_6)$$

$$\text{CO}_2 \text{ formed} = \text{CH}_4 + 2(\text{C}_2\text{H}_6)$$

By extending this scheme and assuming the presence of another paraffin e.g., propane, we get three simultaneous equations which may be solved from the same analytical data used before, yielding results which are correct if the first assumption is correct but which, in general, are indeterminate.

Several analyses of the gases obtained early in the work were made but on account of air leakage in the gasometer the results obtained were misleading. The following is the average of results obtained under satisfactory conditions, from gas evolved at a maximum temperature of 550°.

TABLE XIV.

Gas from Danville Electric Mine Coal.

H ₂ S*	CO ₂	Illum.	Co	H ₂	C ₂ H ₆	CH ₄	N ₂	B. T. U.
3.2	5.7	8.3	5.2	5.0	14.4	51.4	5.7	1032

The computed heat value of this gas 1024 B.T.U. agrees closely with that determined experimentally. Heat values of the different gases as given by Abady³⁶ were used as the basis of

*The low H₂S content may be explained by the fact that the gas had stood over water for some time.

calculation. According to J. H. Coste³⁷ it has been found from Julius Thomsen's figures that the average calorific value of the unsaturated hydrocarbons is equivalent to that of propylene.

Residue (10), from Carterville coal, coked at a maximum temperature of 500°, on being redistilled in a small retort at 1100°, yielded a gas having the following composition:

TABLE XV.

Gas from Residue (10)							computed heat
H ₂ S + CO ₂	O ₂	Illum.	CO	CH ₄	H ₂	N ₂	value B. T. U.
4.3	0	2.7	9.9	47.3	30.2	5.6	677

On comparing the gas evolved from coal heated to 550° (Table XV) with that obtained from the coke residue, it may be seen that the latter with its high methane and hydrogen content is far more likely to burn with freedom from smoke than the former.

EXPERIMENTAL

Second Series: Briquetting Tests.

Early in the course of the preceding work, methods putting the coke residues into a form allowing convenience and economy in handling were seriously considered. One of the first attempts to accomplish this purpose, while directly proving to be utterly impracticable, nevertheless furnished some valuable information in regard to the properties of coal while in the state of fusion.

The apparent plasticity exhibited by the coal during certain stages of the treatment suggested the idea of compressing

36. Gas Analyst's Manual. p. 521 (1902)

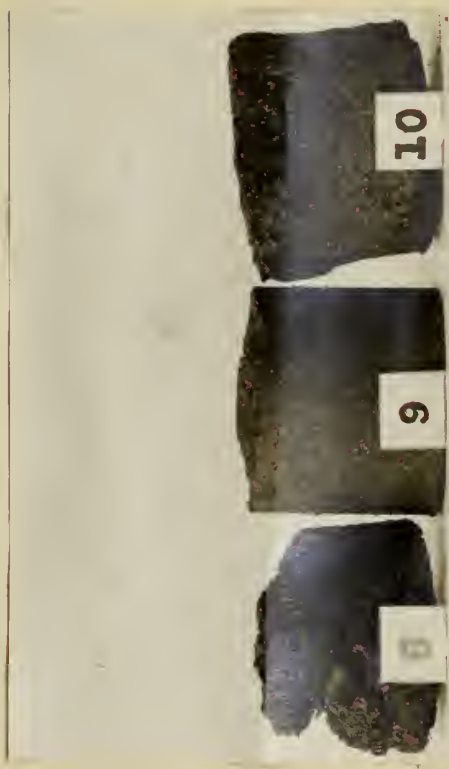
37. Chemical Engineer. Feb. 1911.

it into a briquette at the time when it would most easily yield to pressure and when it would presumably cohere without requiring an artificial binder. Accordingly, a cupel press of 500 lbs. capacity was provided and the retort was charged with Danville Mine coal. At the time of maximum evolution of gas the heat was suddenly shut off and the retort quickly opened. It was found at this point that the outer and hotter portion of the mass was hard and unyielding. A soft inner core was discovered, however, and portions of this were put into the press. The resulting briquette is shown in Fig. (2), No. 8. The escaping gases have swelled it up like a biscuit. Determinations of volatile matter showed that this constituent had been reduced very little from 38% to 30%. In short the state of fusion seems to exist in the early stages of distillation but disappears before the process has proceeded far.

In this connection it is interesting to note that Groves and Thorp³⁸ in a chapter of their work on fuels which had escaped our notice until after our own work had been done, describe in great detail and to considerable length a process ascribed to Sir Henry Bessemer, for making a "patent" fuel. The principle involved is identical with that one just described. In response to an inquiry concerning its success the Bureau of Mines writes under date of April 6, 1911.

"The method, apparently, has no chance for practical success with ordinary bituminous coal, on account of the low percentage of natural binding material found in this fuel..... As no references have ever come to the notice of the briquetting engineer of the bureau, which show any practical application of

38. Chem. Tech. Vol. I, p. 216. (1889)



Briquetting Tests.
Fig. 2.

Bessemer's process, it may safely be said that it was merely an hypothesis of Bessemer's, that coal could be briquetted in this manner, and further facts did not confirm his idea".

This explanation for the failure of the process does not seem to us to be the correct one, however. As we shall show later, many bituminous coals have more than enough binding material to make a firm briquette.

With a view to modifying the method used in the first test by applying pressure during the whole time of heating, a special coal container was devised.

Apparatus. - A, Plate II, is an iron cylinder, 8" by 4", fitted with a screw caps B and B', which receive the coal. The movable piston C to which is attached a long rod D, is pressed against the charge by tightening the nuts E E. The cylinder is perforated with small holes to allow the escape of gases. This contrivance is fitted into the retort originally used and yeast is applied as before.

No. 6 (Fig. 2) shows the results obtained when pressure is applied slowly during the entire heating period. The outer portions passing through the temporary state of fusion soon harden and form a wall which resists external pressure. The inner core, therefore, is extremely porous. When sufficient pressure is applied the outer part fractures and, as in this case, the residue comes out broken up into small pieces. The coke shown in the figure is from the ^{coal from the Barry Co} Majestic coal mine. The specific gravity of the outer portions of the mass is .733 against .652 when coked by ^{the} our first method. ^{without pressure}

It was evident, therefore, that in order to get a firm block, pressure must be constant. In the next run the charge was rammed into the cylinder and the piston was screwed up tightly but not moved after heating had begun. The resulting column cohered well and showed the same increase in specific gravity as the one mentioned above. (25% increase in specific gravity?)

In one of the earlier tests of this series with Danville mine coal, the extreme fusibility of this type was again demonstrated. As the piston was slowly forced in, pencils of bituminous matter were squeezed out through the holes of the cylinder. Fig. () gives a view of some of these nodules. The fact that there was a selective separation of bitumen is proved by a comparison of the ash values, the residue as a whole having 13%, the special exuded portion residue, 8%.

The readiness with which the cementing material ran to waste seemed to indicate that the coal contained a superfluous amount of it - more than was necessary for binding itself together. The correctness of this view was shown by a series of runs in which crushed gas house coke and anthracite were heated with varying amounts of bituminous coal.

No. 7 shows the hard firm product resulting from the mixture of equal parts of Majestic bituminous coal and gas house coke, both crushed to 20 mesh. Equally good results were obtained in the next run with seventy five percent of the coke and only twenty five percent of Danville Electric coal. In like manner powdered anthracite and bituminous coal ratios varying from 1 : 1 to 3 : 1 were firmly cemented together. Pitchy material no longer

exuded from the retort, being absorbed seemingly by the added substance.

One of the essential factors in this scheme for briquetting loose infusible material with bituminous coal is the use of the press for keeping the two substances in close contact. Because of the difficulty of applying such a contrivance in industrial work, attempts were made to attain the desired end by using temporary binders - that is, substances which might hold the particles together closely until the permanent coal binder could relieve them.

Mixtures of Danville mine coal and Danville mine residue No. (17) in the proportion 3 to 1 were thoroughly moistened with water and pressed (1) in the cupel machine and (2) in a testing machine up to 1000 lbs. per square inch. Neither of the briquettes survived the subsequent heating, being evidently disintegrated by the escaping steam. The same effect, though to a much less degree, was noted when coal tar was employed. The resulting briquette retained its shape but was rather soft and friable. Crude molasses, of all the materials tried, proved to be the best for this purpose. Different percentages of the molasses, ranging from five to fifteen were tested out at different times. Below ten, the strength of the briquette was much diminished. No. (9), Fig. (2), is a 3 to 1 mixture of Danville mine residue (17) and fresh Danville mine coal, both ground to 20 mesh, first bound with 11% of molasses and then pressed in the cupel machine. The cake was next heated in the retort under the atmospheric conditions of all the preceding runs. No. (9), two inches high and two inches in diameter, has a crushing strength of 550 pounds per square inch. No. (11) shows anthracite

briquettes made in the same way. They have a specific gravity of 1.02 and crush at 650 pounds per square inch.

Some attempts were made to supply the retort with an inert atmosphere and at the same time to provide a temporary binder, by saturating the coal to be tested with crude petroleum. Heat was applied to the retort but no steam was turned on. The briquettes made in this way (No. 10, Fig. (2)) are poorly cemented and extremely friable, showing evidence of having been puffed out by expanding gases. The idea deserves further testing, however, under modified conditions. Much of the oil used was recovered in the course of the distillation.

SUMMARY

The heavy hydrocarbons of a coal may be so far removed by heating it to temperatures of about 500°, that the residue may be burned by ordinary methods with the absence of smoke.

A large percentage of the sulphur of the coal is retained by the coke residue. Low temperatures do not cause the decomposition of iron pyrites.

Any oxidation of the coal which may take place at ordinary temperatures during storage, or in the process of coking reduces or may even destroy the coking property.

The temperatures at which coking conditions are determined occupy a range of from 400° to 500°.

Most coals contain more cementing material than they need to bind their own matter together into coke. Bituminous coals may be used as binders if means are used to keep the materials together until fusion can take place. The fact that relatively small amounts of molasses will produce relatively strong cokes is a confirmation of the general proposition that the coking property depends upon the presence of comparatively small amounts of the right kind of material.





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